

# Argonne National Laboratory

## LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID BED FLUORIDE VOLATILITY PROCESSES

### Part VI

- A. The Absorption Spectrum of Plutonium Hexafluoride
- B. Analysis of Mixtures of Plutonium Hexafluoride and Uranium Hexafluoride by Absorption Spectrometry

by

Martin J. Steindler and  
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## A. Introduction

The properties of plutonium hexafluoride are of interest both from a fundamental viewpoint related to the properties of hexafluorides of the transition elements, and from an applied viewpoint related to separating processes for spent reactor fuels.

The Fluoride Volatility Process utilizes the volatility of the most volatile fluorides to obtain a separation of the actinides from fission products by connection with the separation process. The spectral properties of plutonium hexafluoride have been investigated to evaluate the applicability of spectral data to the analysis of gaseous mixtures containing plutonium hexafluoride. Owing to the fact that no adequate data on the molar absorptivity indices at various wavelengths exist, a detailed determination of the spectrum of gaseous plutonium hexafluoride was carried out in the ultraviolet, visible, and the near-infrared regions.





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SUPPORT OF FLUID BED FLUORIDE  
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Part VI

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- B. Analysis of Mixtures of Plutonium Hexafluoride and Uranium Hexafluoride by Absorption Spectrometry

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ABSTRACT

The absorption spectrum of gaseous plutonium hexafluoride was determined over the range of wavelengths from 2000 Å to 26,000 Å, and molar absorptance indices were calculated. A test of the spectral method of analysis of plutonium hexafluoride in mixtures of plutonium hexafluoride and uranium hexafluoride was made. The results indicate that plutonium hexafluoride may be determined in mixtures containing uranium hexafluoride by use of a spectral method although care is required to pretreat the cell windows to avoid reaction with plutonium hexafluoride.

I. THE ABSORPTION SPECTRUM OF PLUTONIUM HEXAFLUORIDE

A. Introduction

The properties of plutonium hexafluoride are of interest both from a fundamental viewpoint related to the properties of hexafluorides of the transition elements and from an applied viewpoint related to separations processes for spent reactor fuels.

The Fluoride Volatility Process utilizes the volatility of the pertinent fluorides to obtain a separation of the actinides from fission products. In connection with the separations process, the spectral properties of plutonium hexafluoride have been investigated to evaluate the applicability of spectral data to the analysis of gaseous mixtures containing plutonium hexafluoride. Owing to the fact that no adequate data on the molar absorptance indices at various wavelengths exist, a detailed determination of the spectrum of gaseous plutonium hexafluoride was carried out in the ultraviolet, visible, and the near-infrared regions.





## B. Experimental

The plutonium hexafluoride used in the determination of the spectra was prepared by the reaction of plutonium dioxide or plutonium tetrafluoride and elemental fluorine at about 550°C in nickel equipment.<sup>(1)</sup> The volatile plutonium hexafluoride was collected in a trap cooled to -80°C and purified by trap-to-trap vacuum distillation.

Prior to each spectral determination, the fluorine formed in the decomposition of plutonium hexafluoride by its own alpha radiation was removed by evacuation while plutonium hexafluoride was cooled to -80°C. The purity of the samples was determined by vapor pressure measurements at several temperatures. In all cases, the measured vapor pressures agreed with those reported in the literature.<sup>(2)</sup>

Spectral cells were constructed from 1  $\frac{1}{4}$ -in.-diameter Monel pipe of various lengths, threaded at each end to receive a brass retaining ring which held a Teflon gasket, a 3-mm-thick quartz window, and another Teflon gasket. Cell lengths of 1, 5, and 10 cm were used. A small valve\* containing a flare fitting was welded into the body of the cell. Figure 1 shows the construction of the spectral cells.

Prior to use, each cell was thoroughly cleaned and checked for leaks with a helium mass-spectrometer leak detector. In addition, each cell was treated with elemental fluorine at room temperature for several hours, followed by treatment with plutonium hexafluoride for 15 min before being used with plutonium hexafluoride.

Samples were introduced by expansion of the gas into the evacuated cells. In all instances, the time plutonium hexafluoride was in contact with the spectrophotometer cells was kept to a minimum to avoid deposition of plutonium tetrafluoride on the quartz windows. It was observed, however, that even with these precautions, a small amount of powdered plutonium tetrafluoride was present in the cell after a few determinations. The absorbance of the empty cells in the ultraviolet region usually increased slightly with each exposure to plutonium hexafluoride. The absorbance of the empty cell in the visible and near-infrared regions remained unaffected by pretreatment and exposure to plutonium hexafluoride.

Auxiliary equipment used in this work consisted of a vacuum manifold, storage vessels and traps, all constructed of nickel. Except for the valves used on the cells, valves with nickel diaphragms\*\* were used throughout. The major portion of the equipment was housed in a Blickman Type K hood which had been modified for use with plutonium by replacement of the

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\* Hoke type 1479.

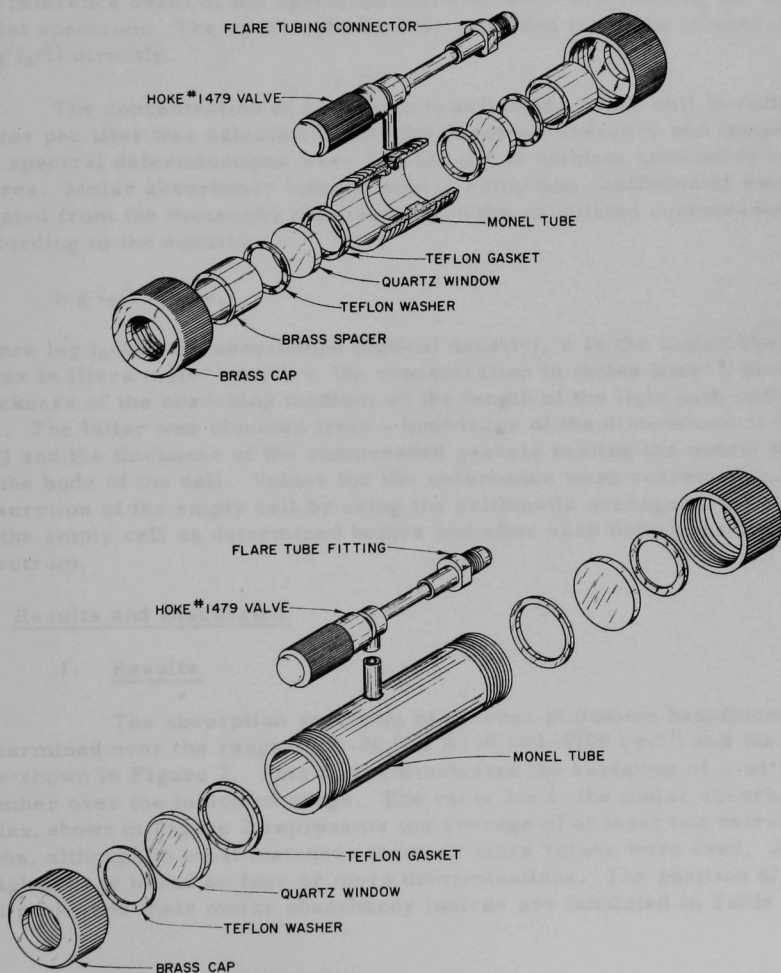
\*\* Hoke type 413A or type 413.



sliding front with a plastic panel containing three glove rings.<sup>(3)</sup> A  $\frac{1}{4}$ -in. nickel tube, terminating outside the hood in a valve and flare fitting, was used to attach the spectral cell to the apparatus. Although the cell was repeatedly disconnected from the apparatus at the flare fitting, use of careful experimental techniques avoided any detectable quantities of plutonium from entering the room.

Figure 1

SPECTRAL CELLS FOR USE WITH CORROSIVE GASES  
TOP FIGURE - 1-cm CELL; BOTTOM FIGURE - 10-cm CELL







Pressures were determined by use of a Booth-Cromer<sup>(4)</sup> pressure transmitter and self-balancing relay which was operated as a null indicator and was connected to a Heise precision gage.

A Cary, Model 14 double-beam, recording spectrophotometer was used for this work. The wavelength calibration of the instrument was checked against a mercury arc and was found to deviate only very slightly from the literature values reported for the mercury arc.<sup>(5)</sup> In order to counteract the increasing absorption by the empty cell, particularly in the ultraviolet, an empty cell which had been exposed to plutonium hexafluoride was used in the reference beam of the spectrophotometer when determining the ultraviolet spectrum. The spectrophotometer recorded the value of absorbance ( $\log I_0/I$ ) directly.

The concentration of plutonium hexafluoride in the cell in units of moles per liter was calculated from the observed pressure and temperature. All spectral determinations were carried out at ambient laboratory temperatures. Molar absorptancy indices (molar extinction coefficients) were calculated from the measured absorbance and the calculated concentrations, according to the equation

$$\log I_0/I = \epsilon \ell c,$$

where  $\log I_0/I$  is the absorbance (optical density),  $\epsilon$  is the molar absorptancy index in liters mole<sup>-1</sup> cm<sup>-1</sup>,  $c$  the concentration in moles liter<sup>-1</sup>, and  $\ell$  is the thickness of the absorbing medium or the length of the light path in the sample. The latter was obtained from a knowledge of the dimensions of the nickel cell and the thickness of the compressed gaskets sealing the quartz windows to the body of the cell. Values for the absorbance were corrected for the absorption of the empty cell by using the arithmetic average of the absorbance of the empty cell as determined before and after each determination of the spectrum.

## C. Results and Discussion

### 1. Results

The absorption spectrum of gaseous plutonium hexafluoride was determined over the range 2000-26,000 Å (50,000-3900 cm<sup>-1</sup>) and the results are shown in Figure 2. This figure illustrates the variation of  $\epsilon$  with wave number over the indicated range. The value for  $\epsilon$ , the molar absorptancy index, shown in Figure 2, represents the average of at least two determinations, although in most instances three or more values were used. All peak heights were based on four or more determinations. The position of principal peaks and their molar absorptancy indices are tabulated in Table 1.





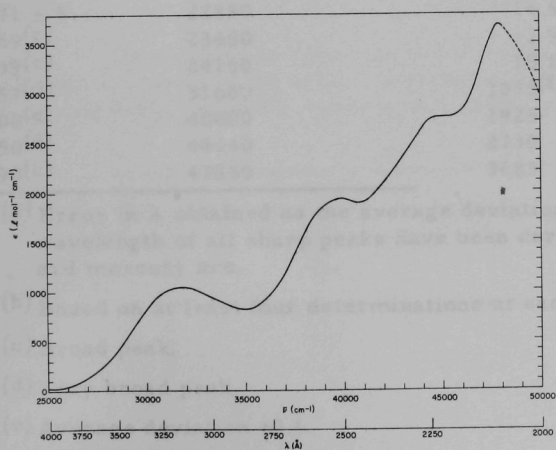
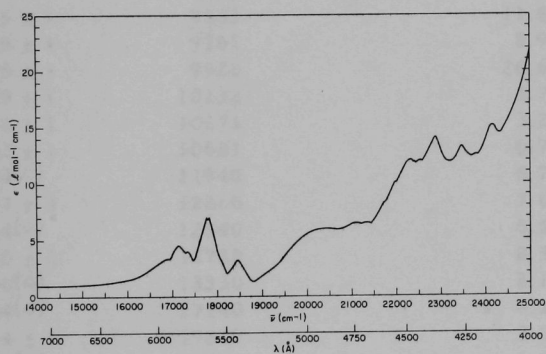
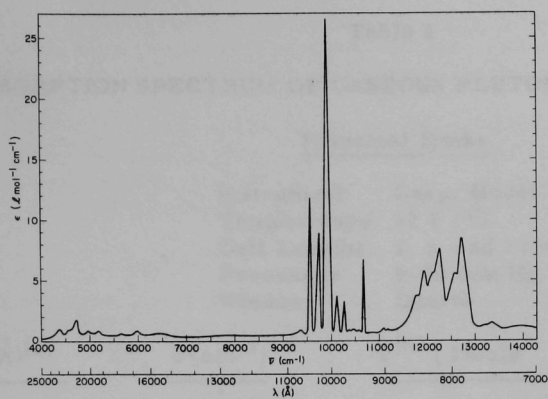


Figure 2  
ABSORPTION SPECTRUM OF  
GASEOUS PLUTONIUM  
HEXAFLUORIDE



Table 1

## ABSORPTION SPECTRUM OF GASEOUS PLUTONIUM HEXAFLUORIDE

Principal Peaks

Instrument: Cary, Model 14  
 Temperature:  $22 \pm 1^\circ\text{C}$   
 Cell Lengths: 1, 5, and 10 cm  
 Pressures: 5-90 mm Hg  
 Window: Quartz

$\lambda$ (Å) <sup>(a)</sup>	$\bar{\nu}$ (cm <sup>-1</sup> )	$\epsilon$ <sup>(b)</sup> (l mole <sup>-1</sup> cm <sup>-1</sup> )	f <sup>(g)</sup>
21150	4728	1.7	$11 \times 10^{-7}$
10435 $\pm$ 1	9583	11.8	$4.3 \times 10^{-7}$
10245 $\pm$ 1	9761	8.9	$5.7 \times 10^{-7}$
10075 $\pm$ 1	9926	26.6(e)	$19 \times 10^{-7}$
9870 $\pm$ 1	10132	3.7	$2.2 \times 10^{-7}$
9734 $\pm$ 1	10273	3.2	$1.6 \times 10^{-7}$
9362 $\pm$ 1	10681	6.7	$1.8 \times 10^{-7}$
8374(c)	11940	5.7	$12 \times 10^{-7}$
8157 $\pm$ 5	12260	7.6	$17 \times 10^{-7}$
7974(c)	12540	6.3	-
7860 $\pm$ 2	12720	8.5	$14 \times 10^{-7}$
7500(c)	13330	2.1	-
5834(c)	17140	4.1	-
5614 $\pm$ 5	17810	7.0	$28 \times 10^{-7}$
5418(c)	18460	3.6	-
4371 $\pm$ 5	22880	14.5	$160 \times 10^{-7}$
4259(c)	23480	13.9	-
4139(c)	24160	15.5	-
3157(d)	31680	1055(f)	$2.7 \times 10^{-2}$
2500(d)	40000	1925	$6.0 \times 10^{-2}$
2250(d)	44440	2730	$9.0 \times 10^{-2}$
2090(c)	47850	3685	-

(a) Error in  $\lambda$  obtained as the average deviation of several scans. The wavelength of all sharp peaks have been corrected by use of a standard mercury arc.

(b) Based on at least four determinations at each peak.

(c) Broad peak.

(d) Very broad peak.

(e) Average deviation  $\pm 0.6$ .

(f) Average deviation  $\pm 80$ .

(g) f =  $(4.60 \times 10^{-9}) \epsilon_{\text{max}} \Delta\nu_{1/2}$  (Ref. 6).



Included in Table 1 are values of  $f$ , the oscillator strength,<sup>(6)</sup> for those bands believed important. These values may be useful to those wishing to carry out a theoretical analysis of the absorption spectrum.

In order to determine the utility of several of the observed peaks for analysis of plutonium hexafluoride in mixtures, Beer's law plots for the absorption at 10,075 Å and 3157 Å were constructed. These, (see Figures 3 and 4) show no significant deviation from linearity.

Figure 3

BEER'S LAW PLOT FOR GASEOUS  
PLUTONIUM HEXAFLUORIDE  
AT 3157 Å

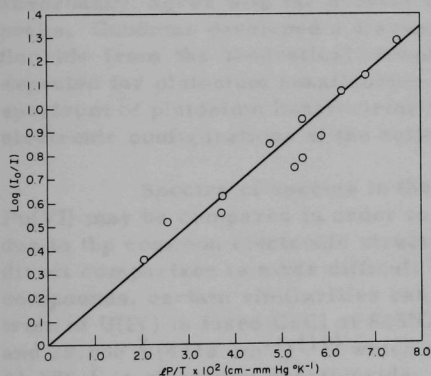
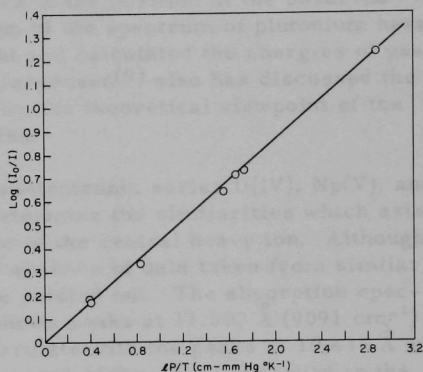


Figure 4

BEER'S LAW PLOT FOR GASEOUS  
PLUTONIUM HEXAFLUORIDE  
AT 10075 Å



108-6874

108-6882

The absorption spectrum in the near-infrared region shows two prominent bands which exhibit observable fine structure. The peak separations observed in the spectrum are tabulated in Table 2, together

Table 2  
PEAK SEPARATIONS FOR SEVERAL BANDS IN THE ABSORPTION SPECTRUM OF GASEOUS PLUTONIUM HEXAFLUORIDE

Band Center (cm <sup>-1</sup> ) <sup>a</sup>	Peak Separation (cm <sup>-1</sup> ) <sup>b</sup>	Pertinent Vibrational Frequency <sup>c</sup> (cm <sup>-1</sup> )	Band Center (cm <sup>-1</sup> ) <sup>a</sup>	Peak Separation (cm <sup>-1</sup> ) <sup>b</sup>	Pertinent Vibrational Frequency <sup>c</sup> (cm <sup>-1</sup> )
4728	175	$\nu_6$ 171	12720	180	$\nu_6$ 171
	178	$\nu_6$ 171		185	$\nu_6$ 171
	224	$\nu_5$ 211		135	-
	223	$\nu_5$ 211		315	$\nu_2-\nu_4$ 320
				145	-
5975	375	-	17810	265	-
	450	-		220	$\nu_5$ 211
9926	230	$\nu_5$ 211		450	$\nu_4 + \nu_5$ 414
	178	$\nu_6$ 171		640	$\nu_1$ 628
	165	$\nu_6$ 171	22880	235	$\nu_5$ 211
	206	$\nu_4$ or $\nu_5$		360	$\nu_2-\nu_6$ 352
	141	-		560	$\nu_2$ 523
	102	-		580	$\nu_2$ 523
	75	-		350	$\nu_2-\nu_6$ 352
	125	-		340	$\nu_2-\nu_6$ 352
	106	-			

<sup>a</sup> Position of either the center of the band or the principal peak in the band.

<sup>b</sup> Determined from a plot of wave number versus molar absorptivity.

<sup>c</sup> Correlation made using only fundamental frequencies ( $\nu_1$  to  $\nu_6$ ) or combinations observed in the infrared spectrum of gaseous plutonium hexafluoride.





with the observed peak separations for those bands which permit such calculations.\* Since it is likely that the observed fine structure represents the vibrational energy levels of plutonium hexafluoride, the data in Table 2 are supplemented by a list of the fundamental vibrational frequencies observed in the infrared region.<sup>(7)</sup>

## 2. Discussion

The only literature reference to the absorption spectrum of plutonium hexafluoride in which experimental data are presented is that of Goodman,<sup>(8)</sup> who showed the observed peaks in the spectrum of plutonium hexafluoride. His results, although not extending very far into the ultra-violet and also not containing any data which permit evaluation of the molar absorptancy, agree with the present work in the position of the observed peaks. Goodman developed a discussion of the spectrum of plutonium hexafluoride from the theoretical viewpoint and calculated the energies of peaks expected for plutonium hexafluoride. Jorgensen<sup>(9)</sup> also has discussed the spectrum of plutonium hexafluoride from the theoretical viewpoint of the electronic configurations of the actinides.

Spectra of species in the isoelectronic series U(IV), Np(V), and Pu(VI) may be compared in order to determine the similarities which exist due to the common electronic structure of the central heavy ion. Although direct comparison is made difficult by absence of data taken from similar compounds, certain similarities can be pointed out. The absorption spectrum of U(IV) in fused CsCl at 825°C shows peaks at 11,000 Å (9091 cm<sup>-1</sup>) and 20,250 Å (4938 cm<sup>-1</sup>)<sup>(10)</sup> which correlate with the peaks at 10,435 Å and 21,150 Å in plutonium hexafluoride. Several of the peaks observed in the spectrum of U(IV) in aqueous solution<sup>(11)</sup> can be correlated with those observed in gaseous plutonium hexafluoride. The spectrum of Np(V) in both aqueous solution<sup>(12)</sup> and in fused nitrate salts<sup>(13)</sup> shows strong peaks at 9830 Å and at 6170 Å, the former corresponding to the 9870 Å peak observed in gaseous plutonium hexafluoride. The interested reader is referred to the cited literature, particularly the work of Goodman, for discussions of the interpretation of the spectrum of plutonium hexafluoride.

## II. ANALYSIS OF MIXTURES OF PLUTONIUM HEXAFLUORIDE AND URANIUM HEXAFLUORIDE BY ABSORPTION SPECTROMETRY

### A. Introduction

The Fluid Bed Fluoride Volatility Process involves the fluorination of oxide fuel elements with elemental fluorine which converts uranium and plutonium to the hexafluorides.<sup>(14)</sup> The hexafluorides are separated from most of the fission products by distillation. In this and subsequent operations, gaseous mixtures of the hexafluorides must be handled, and a simple,

\*The peak separation data shown in Table 2 have been taken directly from the observed data; only the major peaks are listed in Table 1.



nondestructive method of analysis for plutonium hexafluoride in such mixtures is desirable. A method based on the absorption spectra of the hexafluorides was developed for use in the process. Other applications of this method, particularly in laboratory investigations, are believed to be feasible.

## B. Experimental

Plutonium hexafluoride was prepared and purified as outlined previously in this report. Uranium hexafluoride, obtained from AEC sources, was purified in a manner similar to that used for plutonium hexafluoride. The vapor pressure of uranium hexafluoride, used as a criterion of purity, was compared with the literature value.<sup>(15)</sup> Mixtures of plutonium hexafluoride and uranium hexafluoride were made manometrically. In order to obtain a check on the accuracy of the manometric technique, samples of the mixture were hydrolyzed by aqueous nitric acid-aluminum nitrate, and plutonium and uranium were determined in the resulting solution. Plutonium was determined by alpha counting of aliquots of the solution ( $\pm 2$  percent) and uranium was determined by a colorimetric procedure ( $\pm 2$  percent).<sup>(16)</sup> The agreement between the chemical analysis and the manometric data were, in general, satisfactory except at low plutonium concentrations, for which the manometric data are believed to be more reliable.

The determination of the absorbancy of the mixture was carried out in the same manner as described for pure plutonium hexafluoride in Section I of this report. Spectral analyses were carried out both with a Beckman Model DU and a Cary Model 14 spectrophotometer. Comparison of the two instruments revealed little difference in the measured absorbancies of the mixtures ( $\pm$  one percent). One of the peaks used for analysis of the mixtures was the very sharp peak at  $10075 \text{ \AA}$ . The Cary instrument proved more suitable at this wavelength since wavelength adjustments could be made more precisely than in the case of the Beckman.

Two wavelengths were chosen arbitrarily for use in the analysis. The first, at  $3157 \text{ \AA}$ , is applicable for relatively low concentrations of plutonium hexafluoride. Uranium hexafluoride also absorbs at this wavelength,<sup>(17)</sup> and the molar absorbancy index of uranium hexafluoride was determined as  $16 \pm 1 \text{ l mole}^{-1}\text{cm}^{-1}$ . The corresponding value for plutonium hexafluoride is  $1055 \pm 80 \text{ l mole}^{-1}\text{cm}^{-1}$ . The other wavelength, useful for larger concentrations of plutonium hexafluoride, is the sharp peak at  $10075 \text{ \AA}$ , where uranium hexafluoride is transparent. Plutonium hexafluoride has a molar absorbancy index of  $26.6 \pm 0.6 \text{ l mole}^{-1}\text{cm}^{-1}$ .

## C. Results and Discussion

The results of the analyses of mixtures of plutonium hexafluoride and uranium hexafluoride are shown in Table 3 and in Figures 5 and 6. The molar absorbancy index (molar extinction coefficient) of the mixture, shown in



Table 3

DETERMINATION OF THE MOLAR ABSORBANCY INDEX FOR MIXTURES OF  $\text{PuF}_6$  AND  $\text{UF}_6$ 

Instrument: Cary Model 14 or Beckman DU  
 Temperature: Ambient Laboratory ( $\sim 22^\circ\text{C}$ )  
 Window: Quartz, 3 mm thick

Absorbancy ( $\log I_0/I$ )			Cell Length (cm)	Total P (mm Hg)	$\lambda$ (Å)	PuF <sub>6</sub> Content (w/o)		$\epsilon_m$ ( $\text{Lmole}^{-1}\text{cm}^{-1}$ )
Empty Cell before Use	Sample	Empty Cell after Use				PVT Meas	Chem Anal	
0.000	0.070	0.007	1	22.5	3157			54.6
0.007	0.073	0.018	1	20.5	3157			58.2
0.018	0.082	0.027	1	19.5	3157			56.4
0.001	0.987	0.029	1	47.5	3157	9.5	4.5	374.5
0.029	0.878	0.041	1	38.5	3157			401.3
0.041	0.451	0.048	1	21.0	3157			355.3
0.082	0.405	0.088	10	40.5	10075	39.6	36.0	14.7
0.093	0.396	0.110	10	38.0	10075			14.2
0.110	0.325	0.121	10	27.5	10075			14.0
0.121	0.415	0.138	10	37.0	10075			14.2
0.014	0.367	0.043	10	30.0	10075	49.8	50.1	20.8
0.043	0.392	0.057	10	29.5	10075			21.3
0.099	0.390	0.114	10	24.5	10075			21.3
0.060	0.366	0.125	10	18.5	10075	74.5	74.7	27.3
0.125	0.368	0.159	10	17.5	10075			23.8
0.159	0.389	0.176	10	16.5	10075			24.6
0.216	0.450	0.264	10	14.5	10075			26.6
0.264	0.482	0.300	10	14.5	10075			25.3
0.075	0.286	0.087	5	49.5	10075	89.5	86.1	15.3
0.087	0.298	0.112	5	49.0	10075			14.9
0.112	0.252	0.117	5	37.0	10075			13.7
0.123	0.333	0.148	5	47.0	10075			15.4
0.148	0.350	0.174	5	46.0	10075			15.1
0.000	0.594	0.015	1	19.0	3157			569
0.001	0.625	0.040	1	19.5	3157			573
0.000	0.461	0.000	1	17.0	3157			500
0.000	0.647	0.015	1	25.0	3157			471
0.015	0.685	0.018	1	24.0	3157			513
0.000	0.474	0.007	1	45.0	3157	50.3	47.2	193
0.007	0.534	0.027	1	43.5	3157			219
0.027	0.529	0.043	1	43.0	3157			212
0.043	0.490	0.050	1	36.0	3157			227
0.110	0.352	0.132	5	48.0	3157	24.4	16.0	17.7 $\text{UF}_6$ only
0.132	0.414	0.200	5	57.0	3157			16.0 $\text{UF}_6$ only
0.200	0.366	0.229	5	39.0	3157			14.3 $\text{UF}_6$ only
						0		

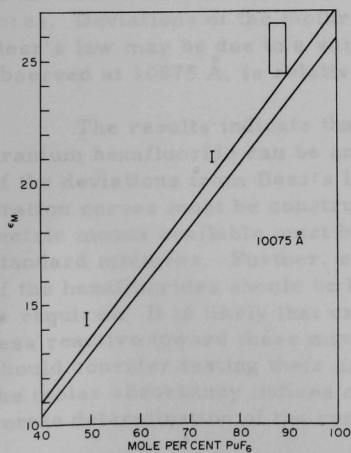
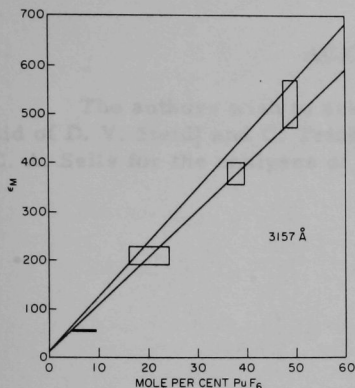


Figure 5  
 $\epsilon_m$  OF  $\text{PuF}_6$ - $\text{UF}_6$  MIXTURES  
 AT 10075 Å





Figure 6  
 $\epsilon_m$  OF  $\text{PuF}_6$ - $\text{UF}_6$  MIXTURES  
 AT 3157 Å



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components determined separately, showing no shift in the position of the peaks and showing the absence of new peaks. It may therefore be concluded that there is no significant interaction between gaseous plutonium hexafluoride and uranium hexafluoride.

It should be noted that the validity of Beer's law for plutonium hexafluoride was not tested in the presence of an inert gas and hence deviations may be anticipated when plutonium hexafluoride is mixed with uranium hexafluoride. The size of the squares shown in Figures 5 and 6 reflect the limits of the determined molar absorptivity indices and the composition of the mixtures. Deviations of the molar absorptivity indices of the mixtures from Beer's law may be due to a variety of causes, although the positive deviation, observed at 10075 Å, is relatively unusual.

The results indicate that mixtures of plutonium hexafluoride and uranium hexafluoride can be analyzed by spectrometric techniques. In view of the deviations from Beer's law, observed particularly at 10075 Å, calibration curves must be constructed. The most accurate chemical or manometric means available must be used to determine the composition of the standard mixtures. Further, exposure of the quartz cell windows to mixtures of the hexafluorides should be kept to a minimum, and careful pretreatment is required. It is likely that crystalline calcium fluoride windows may be less reactive toward these mixtures, and those wishing to apply this method should consider testing their use. Further, more precise determination of the molar absorptivity indices of the pure components, coupled with an accurate determination of the composition of standard mixtures, are required

Table 3, was calculated by use of the determined absorptivity of the mixture, corrected by the average absorptivity of the empty cell. It is realized that simple averaging of the absorptivity of the empty cell may result in a small error, but no other procedure short of eliminating the absorptivity of the empty cell altogether leads to better results. The two straight lines, shown in Figures 5 and 6 represent the spread of the calculated values for the molar absorptivity index of the mixtures, based on the established uncertainties for the molar absorptivity indices of the pure components, and assuming the validity of Beer's law for the mixture.

It was established that the spectrum of a one-to-one mixture of plutonium hexafluoride and uranium hexafluoride is identical with the spectrum of the two com-



to improve the precision of the method of analysis. Finally, it is likely that suitable calibration curves could be developed for mixtures which also contain elemental fluorine.

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